1. Introduction

The pyrazoles are among the most studied heterocyclic aromatic compounds, acting both as simple ligands and incorporated in polydentate ligands [1]. Pyrazole derivatives are the subject of various studies and are used in many different fields, such as pharmacology, biology, and catalysis. They have catalytic [2], anticonvulsant [3], The antifungal activity [4], antibacterial [4-6], antiviral [5, 7], and antiparasitic [5, 8] activities as well as anticancer properties [9], pharmacological activities [10-14] and other different therapeutic actions across a spectrum of diseases [5, 9].

Among the types of membranes, there are liquid membranes which are the first examples of artificial membranes using a complexing agent called a conveyor to extract a species contained in a mixture towards a receptor phase: This mechanism is called facilitated transport. It is known in biologists and physiologists because in living organisms ion transport (Na⁺, K⁺) takes place through cell membranes by proteins or antibiotics [15,16], and solid membranes, or carrier is chemically bonded or trapped in the porosity of the membrane material. The species to be transported pass directly from one site to the other throughout the thickness of the membrane by a series of complexation-decomplexing equilibria. According to Cussler [17], transport through a solid membrane is carried out provided that the transporters are close enough to exchange the species to be transported. If L is the distance between two conveyors and L₀ is the distance that the conveyor can travel around its equilibrium position (mobility of the conveyor), transport takes place if and only if L₀ > L. The selectivity of a membrane depends essentially on the nature of the coordination sites, their number and their topology [18,19]. The stability of the complex formed should not be too high for the cation taken to be released at the membrane / receptor interface. The stability constants K depend on the nature of the conveyor and on the substrate [20,21]. The nature of the anion cotransported with a given cation through a liquid membrane has a great influence on the transport velocities. The latter are a function of the free energy of hydration of the anion and of its lipophilic character [22,23].
2. Materials and methods

In this work, we will prepare the synthesis of new pyrazole tripod and two new monomers incorporating the pyrazole tripods, to prepare a solid membrane, which will be tested in the transport of metals (Cu$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$).

2.1. Synthesis of tripod ligands

The synthesis of the pyrazole tripods T1, T2 and T3, according to the method described in the literature [24-26], was carried out by condensation of two equivalents of 3-chloromethyl-1,5-dimethylpyrazole Pz and one equivalent of 2-aminoethanol and 5-amino-1-pentanol respectively in the acetonitrile in the presence of sodium carbonate according to the following reaction scheme 1.

![Scheme 1: Structure of prepared tripodal ligands](image)

2.2. Synthesis of monomers

The pyrazole tripods prepared can be incorporated into membrane materials by polymerization reactions. Our choice was to fix the methacrylic double bonds on the lateral arm of these tripods. Indeed, the methacrylic monomers are known by a high reactivity in the polymerization reactions. These monomers M1 and M2 are generally obtained by condensation of the corresponding alcohols with methacryloyl chloride in the presence of triethylamine in dichloromethane according to the following reaction (scheme 2):

![Scheme 2: Structure of prepared monomers](image)

2.3. Synthesis of membrane

The presence of complexing ligand in a membrane can confer on it certain special properties: The possibility of separating metal ions by selective diffusion through the membrane. This requires the use of dense membranes. The fluxes of diffusion of the species inside a material are inversely proportional to the crossed thickness (Fick's law), a small thickness of the membrane will optimize the flows. However, films of a few micrometers in thickness are too fragile to be self-supporting, and necessitate the presence of a support which will ensure mechanical stability. Since the facilitated transport membranes are used in the absence of transmembrane pressure, there are no particular requirements on its characteristics.
Our choice was based on a polyacrylonitrile (PAN) base for its low surface porosity, which makes it easier to make deposits and for its good mechanical strength. It has a very high overall porosity with pore diameters greater than about ten micrometers. It is also very permeable to ions and therefore does not limit transport. The diffusion flux of KCl through this support is about 1 mole h⁻¹ m⁻² [27]. The membranes contemplated are dense films resulting from photochemical polymerization of homogeneous solutions of monomers, diluent, crosslinker and photoinitiator spread on a porous polyacrylonitrile (PAN) support.

The formulation which will be spread to the PAN support contains, in addition to the synthesized active monomer (monomer M1), a diluent, a crosslinker and a photoinitiator. Diluent: Since the monomers available to us have a high viscosity, it is necessary to add a diluent to obtain formulations whose viscosity is compatible with the support. Other advantages can be obtained: the use is facilitated and the diluent can provide its intrinsic properties to the membrane.

Crosslinker: A multifunctional, more or less short chain monomer comprising two polymerizable functions at the ends of the chain is generally used. Two essential properties are to be taken into consideration during the development of the membranes: the supple character and the dense character. The first is controlled to the touch and depends essentially on the chemical composition of the formulation forming the membrane and the proportion of each element present. The second is verified by the diffusion of a metal salt NaCl through the membrane of which the grafted transporter has no complexing affinity. Malek [28] carried out a study on the conditions of the synthesis of materials, flexible and dense, incorporating polypyrazolic transporters. By varying the nature and proportions of the diluent and crosslinker, optimum conditions were obtained by using styrene as a diluent and divinylbenzene as crosslinking agent in the proportions of 45% and 5%, respectively, in the formulation.

The photoinitiator used is 2,2-dimethoxy 2-phenyl acetophenone because of its notable absorption in the near U.V [29,30]. Indeed, it decomposes under the action of light with a high quantum yield by releasing very reactive radicals. The formulation contains 3% photoinitiator.

The formulation was coated on a 6 cm square polyacrylonitrile film. The spreading is done using a Hand-Coater threaded rod to form a uniform layer of thickness 6µm. The sample was exposed to UV radiation from a mercury vapor lamp. This light source emits radiation mainly in the range of wavelengths between 250 and 440 nm. The exposure time is 30 seconds, the radiation is carried out at ambient temperature and in the presence of air.

2.4. Characterization of the membrane

The synthesis conditions we have chosen have allowed us to obtain a flexible and dense membrane. Indeed, after twisting the membrane, it resumes its initial shape. We verified this dense character by diffusion of the NaCl through the membrane. The latter is placed between two liquid phases, the first is a solution of NaCl at a concentration of 10⁻¹ M and the second is pure water. Conductivity measurements in the receptor phase show a very low diffusion of the salt through the synthesized membrane, unlike the PAN support where salt diffusion is marked (Figure 1).

![Figure 1: Evolution of the conductances in the receptor phase](image-url)
2.5. Study of the facilitated transport of Cadmium (Cd(II)), Lead (Pb(II)) and Copper (Cu(II)):

2.5.1. Description of the experimental setup

The membrane studied is that prepared from the monomer M1. The membrane is placed between the two halves of the measuring cell and the seal of the assembly is ensured by two teflon seals. The two aqueous phases are agitated by magnetic bars. The scheme of the mounting used is shown in Figure 2. Each compartment has a volume of 90 cm$^3$ and the surface of the membrane in contact with the two aqueous phases is 4π cm$^2$.

The membrane is systematically washed before being tested by filling the two compartments of the cell with distilled water.

![Figure 2: Scheme of the mounting used.](image)

2.5.2. Study Conditions

Transport experiments are carried out using a solution of metal nitrate (Cu(NO$_3$)$_2$, Cd(NO$_3$)$_2$ and Pb(NO$_3$)$_2$) as a source phase at a concentration of 10$^{-2}$ M. The duration of the study is of 24 hours. The passage of the cations into the receptor phase is followed by conductimetric measurements. The conductivity measurements are carried out using an AMEL Model123 conductivity meter equipped with an AMEL192 electrode (K=0.98 cm$^{-1}$).

3. Results and discussion

We have followed the evolution of the conductance of the compartment initially containing pure water, the second being filled with a solution of lead nitrate, cadmium nitrate or copper nitrate at a concentration of 10$^{-2}$ M. The study of the individual transport of the three cations shows a diffusion of Pb$^{2+}$, Cd$^{2+}$ as well as Cu$^{2+}$. The results of these measurements are shown in Figure 3. It is observed that the transport of Pb$^{2+}$ and Cd$^{2+}$ through this membrane is faster than that of Cu$^{2+}$.

![Figure 3: Transport of cations through the membrane.](image)

The evolution of the conductances in the receptor phase is very important in the case of the cation Pb(II) and Cd(II) which have values greater than 650 μs and 550 μs respectively, whereas in the case of Cu(II) the conductance reaches a value of only 400 μs and we note a linear variation of the conductances as a function of time, the ratios of the fluxes are:

\[
\frac{F_{\text{Pb}}}{F_{\text{Cu}}} = 4.5 \quad ; \quad \frac{F_{\text{Cd}}}{F_{\text{Cu}}} = 4.2 \quad ; \quad \frac{F_{\text{Pb}}}{F_{\text{Cd}}} = 1.1
\]
These values show a priori that the membrane is selective to the transport and extraction of heavy metals Pb^{2+} and Cd^{2+} relative to Cu^{2+}.

4. Experimental partie

The \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on a Bruker 300 instrument (operating at 300.13 MHz for 1H, 75.47 MHz for 13C) spectrometer. Chemical shifts are reported in parts per million (ppm). The band positions on Infrared Spectra (IR) are reported in reciprocal centimeters (cm\(^{-1}\)) on a Shimadzu infrared spectrophotometer using the KBr disc technique. Mass spectra (MS) were obtained by using electrospray ionization (ESI) technique. Melting points were obtained using the capillary tube method with an Electrothermal 9100 apparatus. The conductivity measurements are carried out using an AMEL Model123 conductivity meter equipped with an AMEL192 electrode (K=0.98 cm\(^{-1}\)).

4.1. Synthesis of ligands pyrazol

To a mixture of (1.42 g, 13.8 mmol) of 5-amino-1-pentanol and (7 g, 66 mmol) of sodium carbonate in 200 ml of acetonitrile was added slowly a solution of (4 g, 27.6 mmol) of 3-chloromethyl-1,5-dimethylpyrazole in 150 ml of acetonitrile. The mixture was stirred under reflux for 5 hours. The solid material was filtered and the filtrate was concentrated under reduced pressure to give a 75% yield of product. The residue was purified on alunina column with (CH\(_2\)Cl\(_2\)/EtOH: 98/2) as eluent.

Product dialkylayltion \(\text{T2:} \) 5-{bis(1,5-diméthyl-1H-pyrazol-3-ylméthyl)amino}pentan-1-ol, a reddish viscous product is obtained, with a relative yield of 40%. \(\text{RF:} \) 0.8 (CH\(_2\)Cl\(_2\)/EtOH: 98/2). \(^1\)H NMR (CDCl\(_3\)) ppm: 1.35 (m, 2H, HOCH\(_2\)CH\(_2\)-CH\(_2\)-); 1.60(m, 2H, NCH\(_2\)-CH\(_2\)-); 2.10 (m, 2H, HO-CH\(_2\)-CH\(_2\)-); 2.28 (s, 6H, 2CH\(_3\) ); 2.91 (t, 2H, N-CH\(_2\) ); 3.68 (q, 2H, J=6.42Hz); 3.79 (s, 6H, N-CH\(_3\) ); 4.45 (s, 4H, Pz-CH\(_2\)-N); 5.95 (s, 2H, HPz).

\(^{13}\)C NMR (CDCl\(_3\)) ppm: 11.18 (CH\(_2\)Pz); 21.74 (HO(CH\(_2\))-CH\(_2\)-); 22.69 (N-(CH\(_2\)-CH\(_2\)-); 31.28 (HOCH\(_2\)-CH\(_2\)-); 36.61 (CH\(_2\)-N); 55.02 (CH\(_2\)-N); 58.57 (PzCH\(_3\) ); 60.95 (HO-CH\(_2\)-); 109.57 (CPzH); 138.43 (CPz(CH\(_3\) ); 140.40 (CPz(CH\(_3\) )). IR (KBr, v(cm\(^{-1}\))): 3320( OH); 2920 (CH); 1620(C=C); 1530(C=N); 1450; 1350; 1290; 1170; 1070; 1020; 990; 940; 720. m/z: 320 [M+H].

Product trialkylation \(\text{T3:} \) 5-hydroxy-N,N,N-tris(1,5-diméthyl-1H-pyrazol-3-ylméthyl) pentan-1-amin, a yellowish solid is obtained, with a relative yield of 60%. (F\((\text{C})\text{=75-77} \) (CH\(_2\)Cl\(_2\)/EtOH)), \(R_f \) = 0.2 (CH\(_2\)Cl\(_2\)/EtOH: 98/2). \(^1\)H NMR (CDCl\(_3\)) ppm: 1.28 (m, 2H, HOCH\(_2\)CH\(_2\)-CH\(_2\)-); 1.53(m, 2H, CH\(_2\)-CH\(_2\)-); 2.05 (m, 2H, HOCH\(_2\)-CH\(_2\)-); 2.24 (s, 9H, CH\(_3\)); 2.87 (t, 2H, NCH\(_2\)); 3.60 (t, 2H, HOCH\(_2\), J=5.6Hz); 3.75 (s, 9H, CH\(_3\)); 4.38 (s, 6H, Pz-CH\(_2\)-N); 6.52 (s, 3H, HPz).

\(^{13}\) C NMR (CDCl\(_3\)) ppm: 11.57 (CH\(_2\)Pz); 22.12 (HO(CH\(_2\))-CH\(_2\)-); 23.11 (N-CH\(_2\)-CH\(_2\)-); 31.57 (HOCH\(_2\)-CH\(_2\)-); 36.97 (CH\(_2\)-N); 55.39 (CH\(_2\)-N); 59.01 (PzCH\(_3\) ); 61.28 (HO-CH\(_2\)-); 110.05 (CPzH); 138.78 (CPzCH\(_3\) ); 140.75 (CPzCH\(_3\) ); IR (KBr, v/cm\(^{-1}\))): 3300(OH); 2720(CH); 1560(C=C); 1470(C=N); 1380; 1320; 1200; 1170; 1060; 950; 740. m/z: 428 [M+Cl].

4.2. Synthesis of monomers

A solution containing T1 or T2 and an equimolar amount of triethylamine in dichloromethane is cooled to 0°C. Methacryloyl chloride is added dropwise in slight excess. The mixture is stirred for 6 hours at room temperature. The ammonium salt formed is filtered and the filtrate is evaporated at a temperature not exceeding 40°C. The monomers are purified on an alumina column. The characteristics of each monomer are given below.

Monomere M1: (CH\(_2\)Cl\(_2\)/Ethanol: 97/3), Yield: 35%; Appearance: Yellowish viscous.

\(^1\)H NMR (CDCl\(_3\)) ppm: 1.68 (s, 3H, OC\(_3\)H); 1.98 (s, 6H, PzCH\(_3\) ); 2.53 (t, 2H, NCH\(_2\)-CH\(_2\)-); 3.38 (s, 4H, PzCH\(_3\) ); 3.41 (s, 6H, NCH\(_2\) ); 3.96 (t, 2H, OCH\(_3\) ); 5.18 (s, 1H, HB); 5.63 (s, 2H, PzH); 5.73 (s, 1H, HB).

\(^{13}\) C NMR (CDCl\(_3\)) ppm: 11.02 (CH\(_2\)Pz); 18.20 (OC\(_3\)CH\(_3\) ); 36.22 (CH\(_2\)-N); 55.40 (NCH\(_2\)-CH\(_2\)-); 56.60 (PzCH\(_3\) ); 62.90 (OCH\(_3\) ); 105.70 ((HPz); 126.00 (=CH\(_2\) ); 136.10 (C=C); 138.90 (CPzCH\(_3\) ); 167.55 (C=O).

Monomere M2: (CH\(_2\)Cl\(_2\)/Ethanol: 97/3), Yield: 38%; Appearance: Yellowish viscous.

\(^1\)H NMR (CDCl\(_3\)) ppm: 1.40 (m, 2H, NCH\(_2\)-CH\(_2\)-); 1.60 (m, 4H, NCH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-); 1.90 (s, 3H, CH\(_3\) ); 2.10(s, 6H, PzCH\(_3\) ); 2.35 (t, 2H, N-CH\(_2\)); 3.60 (s, 6H, N-CH\(_3\)); 4.10 (t, 2H, O-CH\(_3\) ); 4.40 (s, 4H, Pz-CH\(_2\)-N); 5.45 (s, 1H, HB); 5.80 (s, 2H, HPz); 6.00 (s, 1H, Ha).

\(^{13}\) C NMR (CDCl\(_3\)) ppm: 11.04 (CH\(_2\)Pz); 18.40 (CH\(_3\)(CO)); 23.60 ((OCH\(_2\))-CH\(_2\)-); 27.70 (N-CH\(_2\)-CH\(_2\)-); 28.80 (OCH\(_2\)-CH\(_2\)-); 36.10 (CH\(_2\)-N); 53.45 (CH\(_2\)-N); 56.60 (PzCH\(_3\) ); 64.50 (O-CH\(_2\)-); 105.70 (HCPz); 124.80 (=CH\(_2\) ); 136.30 (C=C); 138.80 (CPzCH\(_3\) ); 152.60 (CPzCH\(_3\) ); 167.20 (C=O).
Conclusion

In this work, we presented the synthesis of a new tridentate ligands, two new monomers were prepared of a condensation between bipyrazole ligands with methacryloyl chloride and new polymer membrane incorporating pyrazole tripods in their structure. The studied membrane is obtained by photopolymerization of a formulation spread on a polyacrylonitrile support. This formulation contains the methacrylic monomer obtained by esterification of pyrazole alcohols with methacryloyl chloride, styrene and divinyl benzene. The membrane obtained is flexible and dense, and is therefore suitable for use in processes with a diffusion mechanism.

The preliminary study of the facilitated transport of three cations shows that the membrane is selective to the facilitated transport of heavy metals Pb\(^{2+}\) and Cd\(^{2+}\) relative to Cu\(^{2+}\).

References
